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Photothermographic Development Mechanisms in Silver Carboxylate Imaging Materials

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The purpose of this article is to provide a critical review of recent advances in mechanistic understanding of the physics and chemistry of the development process in photothermographic imaging media. Accordingly, it is confined to grayscale imaging media based on silver halide–silver carboxylate formulations. The chemistries of infectious development systems and color photothermographic media are not considered, despite their practical and commercial importance. The literature search on which this review is based was restricted to journal articles and conference proceedings papers; the patent literature was excluded. Distinct differences can be defined between the processes occurring in solvent-based and in water-based media, with consequences for their imaging characteristics.

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Introduction

Silver carboxylate based, photothermographic imaging materials have grown in importance over the past decade, especially for medical imaging applications.[1] Many challenges remain, however, to establishing a comprehensive understanding of the physical and chemical mechanisms by which these thermally developable systems function. At the same time the practical importance of these media has stimulated active, sophisticated research to address questions both of latent image formation and mechanisms of development.

Historically[2] photothermographic media were by and large prepared by dispersing the components in a volatile organic solvent, from which the film or paper was coated.[2] More recently, driven by concerns for manufacturing efficiency and the need to reduce environmental impact, water coated formulations have been developed.[3,4] Recent research[4,5] suggests that both mechanisms both of latent image formation and of development may be significantly different in these two types of photothermographic media.

The purpose of this report is to review recent research on the mechanisms of development which operate in both types of photothermographic silver carboxylate imaging media, to the end of establishing a comprehensive picture of the development process operating in them. It should be understood, however, that owing to the longer history of solvent-based systems, much more is known by way of mechanistic detail of the processes occurring in them. Aspects of development in modern photothermographic compositions have previously been considered in more general reviews, both by the present author[6] and by Cowdery–Corvan and Whitcomb.[2]

The scope of this article is confined to grayscale imaging media based on silver halide–silver carboxylate formulations. The chemistries of infectious development systems and color photothermographic media are not considered, despite their practical and commercial importance. The literature search on which this review is based was restricted to journal articles and conference proceedings papers; the patent literature was excluded. Although the patent literature is often more technologically advanced than the open literature, it is also more difficult to infer mechanistic insights reliably from patent disclosures, which are usually structured in such a fashion as to make the reported results unobvious.

Models–Overview

It seems to be generally conceded now that all the image silver in photothermographic elements comprising silver halide and silver carboxylate comes from the silver carboxylate phase.[1,6,7] In contemporary materials the reducing agent is usually a hindered phenolic compound.[8–11] Considerable recent emphasis has been placed on understanding the electron transfer chemistry of these compounds, as will be discussed further below.

Historically the paradigm for discussing latent image catalyzed reduction of silver under thermal development conditions has been solution physical development, which is well known in conventional silver halide systems.[12] Klosterboer[2] proposed that the reaction occurs in two stages. In the first stage filamentary silver is formed, and he suggested that it may correspond to

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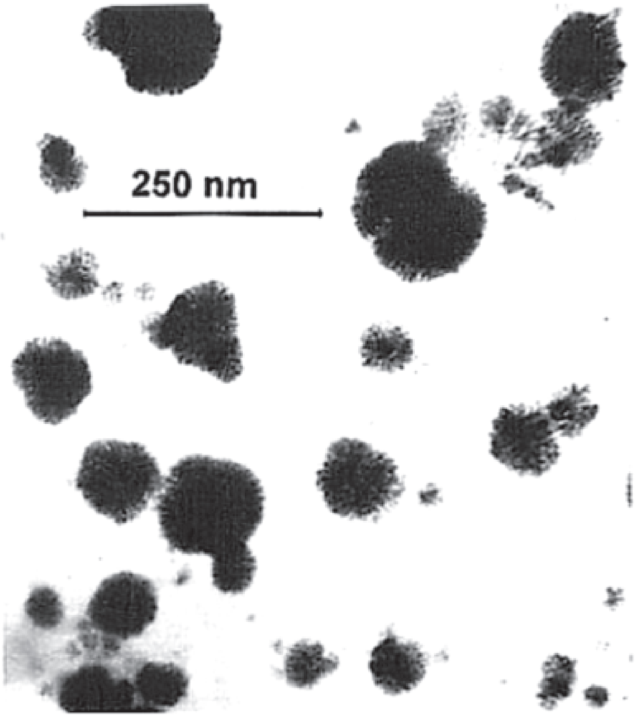


Figure 1. Dendritic silver obtained from development of a photothermographic film (from Ref. 41 by permission of the copyright holder, the Society for Imaging Science and Technology).

extrusion of single silver ionic sheets from silver carboxylate crystals. Subsequently, the morphology of the developed silver changes to an aggregated deposit of nanocrystals,[13,14] or dendritic silver, sometimes called "broccoli silver", which has been associated with operation of the solution physical development mechanism. A transmission electron micrograph (TEM) of a typical dendritic silver deposit formed by development of the image in a photothermographic film is shown in Fig. 1.

One physical interpretation[15] of the two-stage mechanism is that silver cluster growth is, initially, not autocatalytic, owing to the very different electronic properties of small clusters compared to metallic silver,[16] and that a threshold nanoparticle size must be reached before an autocatalytic mechanism can operate. A particle size of 100–200 atoms is thought to correspond to the onset of metallic properties.[17] On the other hand, the functional latent image in typical photothermographic materials is now thought to be the result of absorption of not more than 30–40 photons per AgBr grain.[18,19]

Early on it was thought that thermolysis[2,20,21] of the silver carboxylate also played a role in development. More recently this point of view has been abandoned or ignored, largely because the formation of silver(0) from pure silver behenate, the silver carboxylate most commonly used in formulation of photothermographic media, occurs only above 170°,[22] well above usual development temperatures of 110–130°. Other, shorter chain silver carboxylates may decompose at lower temperature,[23] and silver carboxylate thermolysis may accordingly contribute to fog formation.

That said, it has remained to be elucidated over the past few years, (1) what may be the "soluble" species allowing silver ion to be transported to the growing latent image center where development has been thought to occur, and (2) what is the solvent that allows physical development to occur. With respect to the latter question, Sidelnikov[24] and Usanov[25] independently suggested that carboxylic acid melt may provide the reaction medium, at least when enough carboxylic acid has been formed as a result of the first stage of the development reaction. Use of the Andrade Equation[26] allows estimation of the viscosity of behenic acid melt as 4 cP at 127°, a representative development temperature. This viscosity, only four-fold greater than that of room temperature water, is clearly low enough to support the development reaction.[9] Separation of a behenic acid phase during heating of a model solvent-based construction with polyvinylbutyral binder has been observed by a combination of analytical techniques.[27] As water-based media may be formulated with a binder derived from a styrene-butadiene rubber latex,[3] the same phase separation may not necessarily occur therein.

Klosterboer[2] suggested that silver complexing agents added as "toner" served to solubilize the silver ions. The nature of this chemistry has been the subject of an extensive series of investigations, primarily by Whitcomb and co-workers[28–31] and also Maekawa.[9] Most of the complexing agents are aromatic compounds; given the reported[32] ability of carboxylic acid solvents to selectively solvate aromatic molecules, presumably involving hydrogen bonding to the π-electrons of the aromatic ring,[33] this feature may be critical to the solubility and mobility of the resulting silver complexes.

One consequence of the solution physical development model is the concept of the "sphere of influence". Klosterboer[2] defined the sphere of influence as follows: "It is assumed that only the silver from the silver soap [*sic.*] within a certain radius from a silver halide latent image has the time to diffuse to the latent image and be reduced to image silver during development". This assumption in turn implies that the second stage of the development reaction may be diffusion controlled. Many morphological investigations of developed photothermographic layers, e.g., those reported in Ref. 34, have found physical evidence of the sphere of influence in the form of a zone depleted of silver surrounding each development center in a developed layer of a solvent coated photothermographic film. It should be emphasized that these domains may not be spheroidal at all, but rather appear to reflect the morphology of the silver carboxylate phase. As originally proposed, the effective radius of the sphere of influence was thought to be 0.4–0.6 μm; this range of radii has been supported by theoretical calculations.[35] Experimental studies[34] have inferred a somewhat smaller effective radius, from ca. 0.2 μm to 0.35 μm.[34,35]

The above discussion applies only to solvent-based systems. In recent studies[4,36] on water coated films, on the other hand, no evidence of a physical sphere of influence has been obtained, and the first stage of development has been found to be rate limiting. It has been inferred[36] from these observations that the development reaction is not diffusion controlled in these media, and they support the idea that the mechanism of development is quite different therein. For reasons discussed below, the computational models developed by Ito and co-workers[37] appear more relevant to these water-based films. In this case the sphere of influence concept remains a useful assumption, but it is necessary to allow its size to increase monotonically with development time, consistent with the experimental results of Ohzeki et al.,[36] who showed that in such media size of individual silver deposits increased monotonically with development time.

If we take this sphere of influence as the fundamental imaging element in photothermographic media and apply the common assumption that 50 such elements are required to record one bit of information with adequate signal-to-noise, then (for a representative 5 μm thick photothermographic coating) an upper limit areal information density of 10^9 bits cm^{-2} can be inferred, corresponding to a theoretical resolving power of 1500 cycles mm^{-1}. Accordingly, the ability to record holographic diffraction gratings with spatial frequency up to 1400 cycles mm^{-1} was demonstrated by Usanov and Shevtsov using photothermographic formulations coated on glass plates.[38] In this connection we note that the existence of an exposure dependent induction period in photothermographic development (see below, e.g., Table III) is consistent with the kinetics of operation of holographic developers used with conventional silver halide plates.[39]

Morphology of Developed Silver

As implied above, study of the morphology of silver resulting from the thermal development process has proved critical to reaching the current level of understanding of the development process. Since the morphology of the developed silver formed on thermal development does not, in most cases, correspond to the spheroidal form usually observed in solution physical development of conventional silver halide materials, Usanov[25] has proposed that the solution physical development model may be an oversimplification.

Modern photothermographic materials are usually prepared by the "preformed" method, involving synthesis of the silver carboxylate in the presence of the silver halide phase, a product of conventional silver halide emulsion making technology. Earlier materials had been prepared by-and-large by the "in situ" method, which involved conversion, in part, of silver carboxylate to silver halide using a halidizing reagent. Owing to presence of adventitious halide in reagents and equipment used for synthesis and, in particular, the use of halogenated antifoggants,[40] e.g., pyridinium hydrobromide perbromide, in reality some in situ product coexists with the preformed silver halide in most photothermographic materials.

This fact may be critical to the issue of silver morphology, insosfar as Bokhonov and co-workers have correlated formation of filamentary silver with in situ prepared silver halide and dendritic silver with preformed formulations.[41] The same investigators also noted, however, that in many cases both dendritic and filamentary silver could be observed at the surface of the same silver halide crystal, and also that the initially formed filamentary silver could be a source of the silver occurring in dendrites. These observations are consistent with those reported by Klosterboer[2] from which he inferred a two stage mechanism of development. Historically[42,43] filamentary silver has been associated with direct, so-called chemical, development of silver halide grains, where the silver atoms are produced at a small region of the silver–silver halide interface. If that mechanism operated at early stages of photothermographic development, the silver halide lattice ions reduced in this process would have to be replaced in the lattice with silver ions from the silver carboxylate phase.[41]

Strijckers[44] has suggested that tribromomethyl-functional antifoggants[40] play a key role in determining image silver morphology. Accordingly in the first stage of development reduced silver can, in part, be reoxidized to silver bromide by the antifoggant. Under these conditions filamentary silver forms. When the antifoggant is depleted the competitive reoxidation stops occurring, and the second stage of development, leading to formation of dendritic silver begins. Although supported by some experimental evidence, this mechanism does not necessarily provide a unique explanation for the two stages of development and the observed silver morphologies, which had already been recognized some years before introduction of the tribromomethyl antifoggants.

Chen and co-workers[14] have carried out an elegant multi-dimensional, morphological analysis of developed silver. Again they find the broccoli shaped deposits, with crystalline, filamentary stems and heads comprising agglomerates of nanoparticles. These agglomerates are polycrystalline, which explains, in part, the differences in size estimates, e.g., in Ref. 34, obtained by electron microscopy (ca. 40 nm) and by x-ray diffractometry (ca. 15 nm), which measures monocrystalline domain size. A key result is that filaments are associated exclusively with silver halide grain surfaces, i.e., presumably with latent image sites, consistent with observations of Bokhonov[41] and the models of Berry[42] and of Senchenkov and Chibisov.[43] The filaments are typically 30–50 nm in diameter, while the agglomerates of nanoparticles may be up to 200 nm in diameter. On further heating, the dendritic deposit anneals to dense polycrystals, ca. 60–80 nm in size, a process previously studied by Usanov and Kolesova[7b] and which may be responsible for loss of optical density, i.e., covering power, on overdevelopment. The crystallinity, albeit with short range order, of the developed silver deposit is in strong contrast to the amorphous character of the silver resulting from silver carboxylate thermolysis,[23] which provides further support for the understanding that the latter process does not play a role in image-wise development.

Individual, polycrystalline silver deposits resulting from operation of the development process are typically 3–5 nm in diameter according to Chen and co-workers[14] although somewhat larger particles were reported by Hill et al.,[34] and much larger particles, presumably aggregates of the fundamental nanoparticles were reported by Mizen.[45] All these estimates were obtained by TEM (Transmission Electron Microscopy); smaller estimates derived, e.g., from X-ray diffractometry with Scherrer line width analysis,[46] tend to be misleading owing to the polycrystalline nature[14] of the deposit. Given continuous progress in the capabilities of the TEM technique, the most recent results should be taken as the most reliable in this reviewer's opinion.

Ohzeki and co-workers[36] examined the morphology of the developed silver in water-based photothermographic materials. They found that size of the silver particles scaled both with exposure level and time of development. It is not clear whether these particles are products of an aggregation process or not. Ohzeki[36] proposes that in the water-based materials the development process is reaction, rather than diffusion, limited as in the solvent coated films. On the other hand in solvent coated films unaggregated particle size is relatively constant, and particle number increases with development time and/or level of exposure.[34] In the solvent-based system studied by Hill et al.,[34] it was found that up to 40 different silver particles may result on complete development of the

TABLE I. Activation Enthalpies (eV) for Photothermographic Film Development

	Initiation[34]	Continuation[34]	Autocatalytic[45]
Full-soap film—image	(1.75 ± .14)	(1.84 ± .04)	(1.48 ± .09)
Full-soap film—fog	(1.66 ± .20)	(1.70 ± .15)	(1.39 ± .09)
Half-soap film—image	(2.16 ± .20)	(1.76 ± .20)	—
Half-soap film—fog	(1.26 ± .08)	(1.76 ± .20)	—
Average	(1.71 ± .32)	(1.76 ± .05)	(1.44 ± .05)

TABLE II. Activation Entropies (cal/mol-degree) for Photothermographic Film Development

	Initiation[34]	Continuation[34]	Autocatalytic[45]
Full-soap film—image	*	(+19.0 ± 0.8)	(23 ± 6)
Full-soap film—fog	(+3.0 ± 1.6)	(+17.0 ± 1.4)	(17 ± 8)
Half-soap film—image	*	(+14.8 ± 1.5)	—
Half-soap film—fog	(−15.4 ± 0.8)	(+14.4 ± 1.2)	—
Average	—	(+16.3 ± 1.8)	(20 ± 3)

* Varies with exposure; see below.

sphere of influence of one silver halide grain, and a secondary nucleation process was inferred. Usanov and Kolesova[7b] also observed in quite different formulations that silver nanoparticles could be nucleated under development conditions in the silver carboxylate phase, at sites other than points of contact between silver carboxylate and silver halide. These deposits were consistently amorphous.

Kinetics and Thermodynamics of Development

Despite the fact that development in photothermographic media is a thermally activated process, there appear to be only two reported attempts to measure activation parameters for modern films. Following the paradigm of two discrete stages of development, Hill and co-workers[34] separately measured activation parameters for: (1) the initiation stage, which they took to be characteristic of the induction period for visually detectable image silver, and (2) the continuation stage, corresponding to a more-or-less linear increase in developed optical density, taken to be linear with mass of silver developed, with time. Their data were originally reported as Arrhenius activation energies, E_a (eV). These authors also compared full-soap films, in which all behenate moieties are present as silver behenate, and half-soap films in which equal amounts of silver behenate and behenic acid are formulated into the coating.

Mizen[45] on the other hand, attempted to describe the development kinetics in terms of a single autocatalytic process, characterized by a single autocatalytic rate constant, k_{auto}. The autocatalytic analysis is consistent with the character of both physical[47] and direct[48] development in conventional silver halide systems. From the temperature dependence of k_{auto} this author inferred enthalpies and entropies of activation, ΔH^* (kcal/mol) and ΔS^* (cal/mol-degree), respectively, where (in units of eV) $\Delta H^* = E_a - k_bT$. Data from these two studies are reported in Table I, where all activation energies are presented as ΔH^* in eV.

Entropies of activation, ΔS^*, are reported in Table II. Estimates of ΔS^* may be derived from the Arrhenius pre-exponential factor, A, using

$$\ln A = \ln(k_bT/h) + \Delta S^*/k_b + 1 \tag{1}$$

obtained from Transition State Theory.[49] The two methods of analysis yield somewhat different activation parameters, which is unsurprising, even though both studies were carried out on apparently similar films using the same apparatus. With respect to the entropies of activation, it is well known that the kinetics of the later stages of an autocatalytic reaction can be approximated as a pseudo-first order reaction, with rate constant, k. In this case, it has been shown[50] that

$$k = 0.25\, k_{auto}[\mathrm{A}] \tag{2}$$

where [A] is the concentration of the non-limiting reagent, most likely the developing agent in the case of thermographic development. Under the present conditions, Eq. (2) means that entropies of activation estimated using Eq. (1) will be more positive according to the autocatalytic model by an amount of [2 ln(4/[DH])], where the effective concentration of developing agent, [DH], is not experimentally determined.

The consistently positive estimates of ΔS^* (except for the initiation stage of fog formation in the half-soap film) have been interpreted as suggestive of a unimolecular transition state for the rate determining step in the development reaction.[45] The entropy data also allow us to distinguish mechanistically between fog center nucleation and the other stages of image and fog development. The fact that the activation enthalpies for both the initiation and continuation stages of development are the same for exposed full-soap samples suggests that the autocatalytic treatment of Mizen is appropriate, at least in this case, i.e., there is a continuity of mechanism throughout the course of the reaction, contrary to the proposal of Winkelmann and Mills.[15]

The activation enthalpies are much larger than might be expected for a diffusion process. Contrary to the assumption underlying the Klosterboer model[2] and the inference of Ozheki et al.,[37] the reaction does not seem to be diffusion limited, at least macroscopically.

A different proposal was developed in Ref. 34. Morphological studies[34,44,45] have shown that secondary nucleation events, i.e., nucleation of new silver particles independent of the growing latent image or fog center, are characteristic of the development of solvent-based photothermographic films, but not of water-based films. In the former case, up to 40 secondary nucleation events may occur within one sphere of influence, whose development may be initiated by a single latent image or fog center in the films studied. In the model derived for that situation, the rate of reaction is limited by the rate of these nucleation events, and the process can be described in terms of crystallization theory, e.g., the BNG (Balanced Nucleation and Growth) model,[51] as well as older theories of phase formation.[52] The proposed chemistry has characteristics in common with infectious development as observed in both conventional[53,54] and photothermographic[45] silver systems.

It should be kept in mind that the rate of development of measurable optical density is not necessarily the same as the rate of growth of individual silver particles under development conditions; rather the observable rate may correspond to an increase over time in number of deposited silver particles. The latter limiting case has been found for conventional silver halide media to correspond to cases where the silver reduction reaction is diffusion controlled,[55] and has been shown to apply to the development of solvent-based photothermographic films.[34] Once nucleated, a silver nanoparticle may grow by a diffusion limited process, but this process is fast compared to the rate of nucleation. According to the authors of Ref. 34 the rate of growth of optical density, D, can be related to the rate of increase in the number of nanoparticles, z, in a sphere of influence

$$\mathrm{d}\ln D/\mathrm{d}t = \mathrm{d}\ln z/\mathrm{d}t = k. \tag{3}$$

Equation (3) is of course an approximation, especially insofar as it assumes silver covering power to be independent of developed density. It is consistent with Mizen's[45] presumption of the applicability of autocatalytic kinetics, but not with the computational model of Kong,[35] which, however, does not take secondary nucleation events into consideration. Further precedent for this mechanistic inference is provided by the reduction of silver ion in 2-propanol[56] where autocatalysis corresponds to a time-based increase in number of silver nanoparticles which have catalytically active surfaces. As in the case of solvent-based photothermographic media, nanoparticle size remains more-or-less constant over the course of this reaction.

Therefore, individual silver nanoparticles should not be considered the analogs of silver halide grains in conventional films. Rather, as proposed above, the individual spheres of influence fulfill this role, and for a given time of development the fractional conversion of the silver carboxylate to image silver in a given sphere of influence reflects the level of exposure received by this imaging element. Thus, a photothermographic film can function as an array of multi-level detectors, theoretically capable of improved detective quantum efficiency compared to typical conventional media.[57]

Returning to the question of the growth of individual nanoparticles under development conditions, we consider that the driving force for enlargement of a silver nanoparticle, e.g., by Ostwald ripening or surface chemical reaction, is the reduction of excess surface free energy, ΔG_x, given by the Gibbs–Thompson Equation[58]

$$\Delta G_x = 2\sigma V_m/r \tag{4}$$

where σ is the specific surface energy, V_m is the molal volume of silver, and r is the particle radius.[59,60] Thus

$$\mathrm{d}\Delta G_x/\mathrm{d}r = -2\sigma V_m/r^2 \tag{5}$$

which means that the step-wise free energy change with incremental particle enlargement monotonically decreases with increasing particle size.

According to the electrode model of photographic development commonly used to describe both physical and direct development in conventional silver halide systems,[47] Eq. (4) may be combined with the Butler–Volmer Equation for electrode reaction kinetics, here written for the case where the anodic half-reaction (developer oxidation) is limiting, and supposed to be applicable to the growth of a single silver nanoparticle:

$$\begin{aligned}&\mathrm{d}[\mathrm{Ag}^\circ]/\mathrm{dt} =\\&4\pi r^2 Z[\mathrm{DH}]\exp\{-\alpha[Fe(E_c - E_a)/RT + (2\sigma V_m/r)/k_b T]\}\end{aligned} \tag{6}$$

where Z is a frequency factor (rate constant), α is a symmetry factor ($\alpha \approx 1$), F is the Faraday constant, e is electronic charge, E_c is the electrode potential for the cathodic half-reaction (silver ion reduction), and E_a is the corresponding potential for the anodic half-reaction (developer oxidation). For values of σ typical of silver in aqueous environments,[60] ca. 1000 erg cm^{-2}, the second term in the exponential argument of Eq. (6) becomes inconsequential (≤ 1) for $r = 4$ nm, in agreement with the best experimental estimates for individual nanoparticles formed in photothermographic films.[14]

When this particle size limit is reached, the reaction rate falls below the rate at which silver ion is delivered to the reaction center by diffusion, and the immediate reaction environment becomes supersaturated in reducible silver species. According to phase formation theories[51,52,61] additional nucleation events then occur spontaneously. Mechanistically such nucleation during the course of image development should be indistinguishable from fog nucleation. Thus if nucleation is actually rate determining with respect to the growth of observable optical density, as proposed by Hill et al.,[34] the activation parameters for initiation and continuation stages of both fog and image development should be the same. Table I demonstrates that this inference is correct, at least for full-soap formulations.

Structure and Function of Silver Complexes

Soluble silver complex formation is now accepted as the primary pathway for delivery of carboxylate derived silver ions to the development center, i.e., growing silver nanoparticle.[9,28–31] However, in earlier photothermographic formulations which did not include active complexing reagents, development still occurred. Usanov and Kolesova[7b] proposed that under such conditions, heating silver carboxylates above their first phase transition (ca. 120° for silver behenate), which was subsequently shown by Bokhonov et al.[62] to be a Martensitic transition, allows the silver carboxylate crystals to decompose into spherical micelles which are capable of diffusing in the carboxylic acid melt to the reaction site. In the presence of complexing agents, however, Arrhenius plots of development kinetics[34,45] are smooth over the temperature of this silver carboxylate phase transition, so it is thought that the transition does not gate the development process.

Phthalic acid ($\mathrm{PAH_2}$), 4-methylphthalic acid ($\mathrm{4MPAH_2}$), phthalazine (PHZ), and phthalazinone (PAZ) are the most important complexing agents used in photothermographic formulations.[2,28–31] Phthalimide and succinimide were included as toners in some earlier formulations[7b]; these compounds may also function as complexing agents, albeit weakly. Pyridazone derivatives have recently been designed as silver complexing agents, specifically for photothermographic application.[63]

It is generally accepted that the stoichiometric reaction in $\mathrm{PAH_2}$ or $\mathrm{4MPAH_2}$ containing formulations is

$$2\,\mathrm{Ag(O_2CR)} + \mathrm{PAH_2} \rightarrow \mathrm{Ag_2PA} + 2\,\mathrm{HO_2CR} \tag{7}$$

though this idealized chemical equation is not necessarily descriptive of what occurs in the film. The solid state structure of this insoluble di-silver salt has been determined.[28] Note that free carboxylic acid is released in this reaction, and actual reduction of silver is not necessary to provide sufficient carboxylic acid to serve as a reaction medium, as has been confirmed in elegant studies using atomic force and near-field scanning optical microscopies.[27]

Although a functional film can be formulated with $\mathrm{PAH_2}$ alone, it is more common to combine this complexing agent with PHZ in order to obtain a more neutral image tone. In situ halidized films formulated with $\mathrm{PAH_2}$ alone are reported[64] to exhibit undesirably low values of D_{max}. PHZ and $\mathrm{PAH_2}$ form complexes with each other, e.g., $\mathrm{(PHZ)_2{\cdot}PAH_2}$ and $\mathrm{(PHZ)_2{\cdot}(PAH_2)_3}$,[65] both of which have been isolated and characterized structurally. Interestingly both these complexes melt with decomposition at temperatures close to that of the Martensitic transition of silver behenate or silver stearate, i.e., under development conditions. PAH_2 (or $4MPAH_2$) and PHZ are usually added to photothermographic formulations in an approximate 2:1 ratio, which implies that these reagents may be present in coated films in the form of the 2:1 complex, which then releases the individual reagents on heating to development temperature. This latency of the complexing agents may contribute to the shelf stability of coated photothermographic materials of this type.

PHZ itself reacts with silver carboxylates to form isolable, soluble complexes, e.g., $[Ag(O_2CR)(PHZ)(H_2O)_2]_2$.[28] Analogous, mixed phthalate-PHZ complexes, e.g., $[Ag_2(PHZ)_2(PA)(H_2O)]$, are also known.[28] Maekawa and co-workers[9] have proposed that in the presence of both PHZ and PAH_2 the di-silver phthalate complex forms initially, Eq. (7), and is subsequently converted to a more soluble phthalazine complex, which they formulate as $Ag(PHZ)^+$ or $Ag(PHZ)_2^+$ (or a mixture thereof), based on NMR evidence. Thus

$$Ag_2(PA) + 2\ PHZ \rightarrow 2\ Ag(PHZ)^+ + PA^{2-} \qquad (8)$$

where an analog of Whitcomb's $[Ag_2(PA)(PHZ)]$ complex may be intermediate, and

$$Ag_2(PA) + PHZ \rightarrow Ag_2(PA)(PHZ) \qquad (8a)$$

$$Ag_2(PA)(PHZ) + PHZ \rightarrow 2\ Ag(PHZ)^+ + PA^{2-} \qquad (8b)$$

with the solubility of the ion paired $Ag(PHZ)^+$ species in the fatty acid melt as the driving force for the reaction sequence; research to date has not, however, identified the necessary counterion of the $Ag(PHZ)^+$ cation. Also

$$Ag(PHZ)^+ + PHZ \rightarrow Ag(PHZ)_2^+. \qquad (9)$$

An analog of Whitcomb's[28] phthalazine-carboxylate complex is not excluded by the evidence presented by Maekawa.[9] Thus in the fatty acid (RCO_2H) melt,

$$Ag(PHZ)^+ + RCO_2H \rightarrow Ag(O_2CR)(PHZ) + H^+ \qquad (10)$$

A consensus is emerging that the products of Eqs. (8)–(10) are responsible for the transport of silver ion to the development center with the liquid fatty acid byproduct of Eq. (7) as the reaction solvent in either solvent-based or water-based films.

The coating solvent, whether aqueous or non-aqueous, is, of course, no longer present under development conditions and cannot influence the course of the reaction or the characteristics of the intermediate species. It has, however, been acknowledged that there are significant differences in the development chemistry occurring in solvent- and water-based films, but these may reflect the fact that different polymeric binders are used in each case, and that diffusibility of the species involved may accordingly be different.

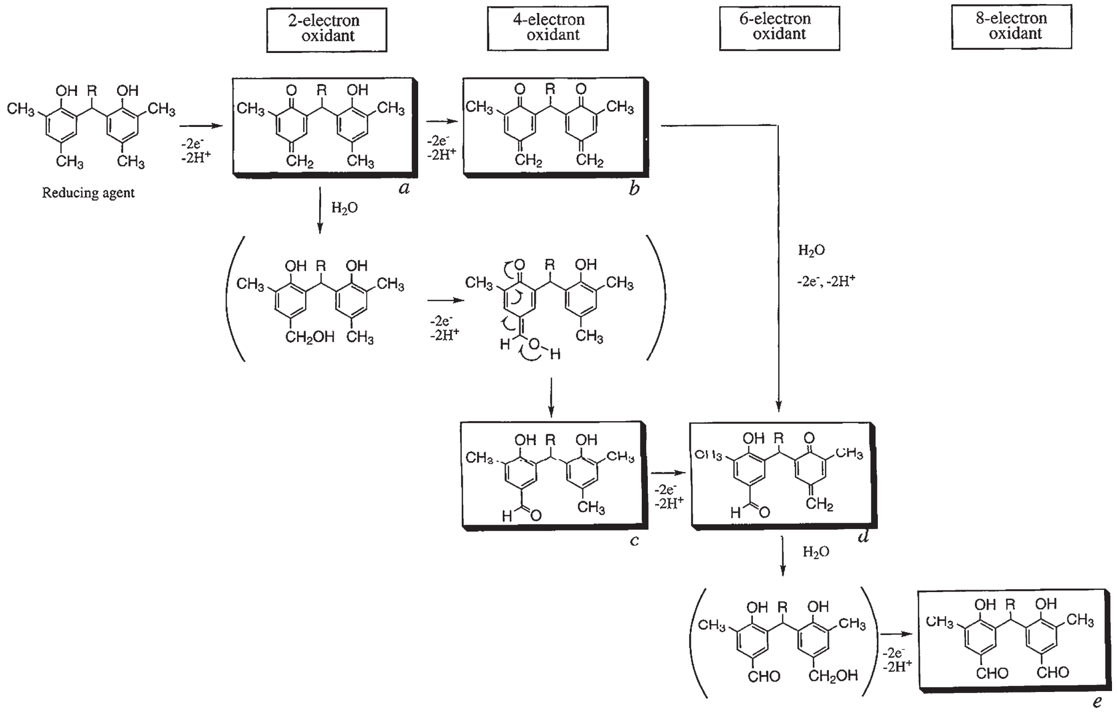
Usanov and co-workers[66] reported that pre-exposure heating to 115° of photothermographic films resulted in a loss of maximum developable density. This temperature is just below the Martensitic transition of silver behenate or silver stearate but above the melting point of free carboxylic acid. This observation may be related to deterioration of sensitometric properties of commercial films during extended shelf storage. The degradation was found to be connected to the presence in the photolayer of complexing agents, phthalimide and succinimide in this case. Formation of unreactive silver complexes was inferred, which implies that not all silver complexes formed thermally from silver carboxylate and the complexing agents are capable of participating in the development reaction. It was further postulated on thermodynamic grounds that this etching of the silver carboxylate phase by the complexing agent is nucleated at the silver halide-silver carboxylate interface. Thus formation of a deposit of unreactive complex also serves to isolate latent image centers from the reservoir of silver ion required for their enlargement into image silver. This chemistry would be expected to occur during development conditions, as well. Thus a certain amount of silver is "wasted" by being trapped in unreactive complexes, formed in competition to the reaction pathway leading to development, and complete utilization of carboxylate silver in image formation is thereby not realized in practice.

Although the structures of the complexes formed under Usanov's conditions were not elucidated, recent work by Whitcomb and co-workers[31] is strongly suggestive of the type of unreactive complexes which may form in PAH_2 containing constructions. These workers have shown that reaction of silver ion with *ortho*-dicarboxylic acids can lead to highly cross-linked, insoluble polymeric complexes. The solid state properties of such complexes are inconsistent with their further participation in the development process.

Developing Agents and Their Reactions

The developing agents typically used in silver carboxylate-based photothermographic imaging systems are sterically hindered *bis*-phenolic compounds.[1,8,67] In principle, these compounds are eight electron reducing agents,[9] but recent work suggests that only the first two one electron oxidation steps may be relevant to the reduction of silver ion in thermally processed films.[10,11] On the other hand, these same authors[11] show that monophenol analogs of the *bis*-phenol developing agents, which are limited to four electron oxidation, are incapable of functioning as developing agents under comparable conditions. A more positive value of the redox potential, $E°$, for oxidation, by ca. 0.1 V, for the monophenolic compounds may account for this observation.[11] An HPLC analysis of developed film samples indicated that the developing agent may undergo two, four, six, or complete eight electron oxidation, depending on exposure level, development time and temperature.[9] The entire eight electron oxidation scheme for a typical *bis*-phenol developing agent is shown in Scheme I.

Akahori and co-workers[11] systematically studied the electron and hydrogen transfer reactions of a series of mono- and *bis*-phenol developing agents. They found that rates of electron transfer quenching of photoexcited acridinium ion by the various developing agents in homogeneous solution were all about the same (diffusion limited). On the other hand, the rates of two electron oxidation, on reaction with *tris*-bipyridyl iron(III), $Fe^{III}(bipy)_3$, correlated with $E°$; the deprotonation of the radical cation formed in the first oxidation step was found to be rate determining.[10] This apparently anomalous result can be rationalized if the first electron transfer step is reversible, and an equilibrium concentration of radical cation is established prior to the rate determining deprotonation. The results of this study can be summarized in Eqs. (11) – (14).



Scheme I. Reaction scheme for eight-electron oxidation of a typical *bis*-phenolic developing agent (from Ref. 9 with permission of the copyright holder, the Society for Imaging Science and Technology).

$$Fe^{III}(bipy)_3 + (bPOH) \rightarrow Fe^{II}(bipy)_3 + (bPOH^{\bullet+}) \quad k_1 \quad (11)$$

$$Fe^{II}(bipy)_3 + (bPOH^{\bullet+}) \rightarrow Fe^{III}(bipy)_3 + (bPOH) \quad k_{-1} \quad (12)$$

$$(bPOH^{\bullet+}) \rightarrow (bPO^{\bullet}) + H^+ \quad k_2 \quad (13)$$

$$Fe^{III}(bipy)_3 + (bPO^{\bullet}) \rightarrow Fe^{II}(bipy)_3 + (bPO) \quad k_3 \quad (14)$$

where k_1, k_{-1} and k_3 are the second order rate constants for the reaction indicated, and k_2 is the pseudo-first order rate constant for the deprotonation step. From the experimental result that deprotonation is the rate determining step in this sequence, it follows that

$$k_2 > k_{-1}[Fe^{II}(bipy)_3]. \quad (15)$$

Steady state treatment of this reaction scheme with both forms of the one electron oxidation product, $(bPOH^{\bullet+})$ and $(bPO^{\bullet})$, as steady state intermediates and using approximation (15) yields the intuitively plausible relationship,

$$d[Fe^{II}(bipy)_3]/dt =$$

$$k_2[(bPOH)]\{k_1[Fe^{III}(bipy)_3]k_1[Fe^{II}(bipy)_3]\}, \quad (16)$$

where the first factor reflects the fact that the deprotonation step is rate determining, and the second factor defines the electrochemical driving force for the reaction according to the Nernst Equation. Insofar as $Fe^{III}(bipy)_3$ may be an appropriate model for $Ag^{I}(PHZ)_2$ the conclusion embodied in Eq. (16) leads us to expect:

(a) a linear free energy correlation, i.e., rate proportional to electrochemical driving force, for photothermographic development; and
(b) pairwise reduction of silver ions to silver atoms.

The former prediction has not been verified quantitatively, to this reviewer's knowledge. Klosterboer[2] states, however, "The stronger the reducing power of the developer the lower the temperature at which the material will develop". The latter prediction may be crucial to the efficient process of secondary nucleation during development, as nearly simultaneous formation of a pair of silver atoms will lead to an Ag_2 molecule, generally thought to be a stable species,[68] and the fundamental nucleus from which nanoparticles evolve, with aggregation processes playing an important role.[69] Mizen's inference[45] that the rate determining step in the sequence of developing reactions must be unimolecular is consistent with the assumption that the deprotonation, Eq. (13), is rate determining under development conditions as well as in homogeneous solution. It is implicit in using the reactions of Eqs. (11) – (13) as prototypes that the one electron reduction of $Ag^{I}(PHZ)_2$ is reversible, i.e., electron transfer is not concerted with dissociation of the complex as previously suggested.[34] This inference is consistent with the reported metastability of micellized silver atoms, sequestered in hetero-crown ether complexing agents,[70] though complexed silver atoms may, in fact, possess considerable ionic character.[71] Analytical characterization of the organic byproducts of development[9] lead to the conclusion that subsequent to the first two electron oxidation of the developing agent, subsequent electron transfer steps also occur in pairs.

The rates of hydrogen atom transfer from the same developing agents to cumylperoxyl radical varied, but did not correlate with $E°$.[11] In this case, the *ortho-t*-butyl substituted *bis*-phenol exhibited anomalously high reactivity, which also proved to be the case for its development of image silver in a photothermographic construction. The authors hypothesized formation of intramolecular hydrogen bonds which stabilize the radical cation, i.e., the one electron oxidation product ($bPOH^{\bullet +}$), and the phenoxy radical ($bPO^{\bullet}$) resulting by deprotonation of the radical cation, Eq. (13), as a principal factor controlling reactivity of these compounds under development conditions. This stabilization is presumably reflected in k_2 of Eq. (16), and must, therefore, be incipient in the transition state of the reaction described by Eq. (13).

Origin of the Characteristic Curve

Solvent-Based Photothermographic Media

Initial attempts to relate photothermographic characteristic curve shape to mechanistic understanding were embodied in the Klosterboer–Rutledge (KR) model.[2,72] In this model the curve shape was presumed to be controlled by the statistics of photon absorption in individual silver halide grains, as had been established for conventional silver halide media.[73] Subsequent attempts to modify the KR model to conform to the observable behavior of real photothermographic films have forced the conclusion that this presumption is untenable.[35,37,74,75]

Experimental and computational studies of development kinetics[34,37,45] all agree on the existence of an exposure dependent induction period for the development reaction. With respect to solvent-based photothermographic media, the continuity of development mechanism over the course of the reaction[45] and the relationship embodied in Eq. (3) imply that exposure controls the number (*vis-á-vis* the size) of catalytic centers formed in a given sphere of influence, i.e.,

$$N = \Phi E \tag{17}$$

where Φ is a quantum yield for latent image center formation, E is exposure, and N is a number density of latent image centers. Like Eq. (3) above, Eq. (17) has to be understood as an approximation valid at exposures below those producing D_{max}, which corresponds presumably to some sort of saturation of response of the photothermographic latent image forming system.

The idea of multiple latent image centers in one sphere of influence is intuitively reasonable:

(a) there are multiple silver halide grains within the volume of any sphere of influence; from Poisson statistics there must be an average of at least four grains in order for every sphere of influence to incorporate at least one grain with >98% probability; and

(b) in addition to pre-formed silver bromide grains, the action of halogenated antifoggants produces additional silver halide deposits in situ, as described above.

Furthermore, formation of multiple latent image centers may be associated with individual silver halide grains in this type of formulation. Eq. (17) has been shown to apply to conventional photographic emulsion grains exposed at the high intensity, short time limit,[76] including conditions of laser flash photolysis,[77] and to silver bromide nanoparticles.[78] Strijckers[79] has also shown that photolytic silver deposits associated with silver halide grains in the presence of silver carboxylate are highly disperse.

For the kinetics of phase formation at z nucleation sites under conditions where a linear free energy relationship applies

$$\Delta S^* = q\Delta S = q(\Delta S^\circ + k_b \ln N) \tag{18}$$

TABLE III. Induction Periods (sec) for Development as a Function of *E* and *T*.

	$E_{rel\text{-}}$ =	0.2	1.0	5.0	20.0	q	r
T = 100°		16.5	11.0	9.9	6.3	0.193	–0.973
105°		8.4	5.5	3.7	2.8	0.239	–0.998
110°		5.2	3.6	3.0	1.9	0.206	–0.984
115°		2.7	2.1	1.6	1.2	0.175	–0.998
						avg. = (0.20 ± .02)eV	
ΔH (eV) =		1.48	1.35	1.42	1.34	avg. = (1.40 ± .06)eV	

$$\Delta S^* = q(\Delta S^\circ + k_b \ln\Phi + \ln E) \tag{19}$$

where ΔS° is the entropy change associated with silver deposition at one reactive center (and whose numerical value accordingly depends on the units of N), and q is a transmission coefficient. Treating the duration of the induction period, t_i, as the inverse of a rate constant[34] we write

$$\ln t_{i\text{-}} = (\Delta H^*/k_bT) - \Delta S^*/k_b \tag{20}$$

so that

$$\ln t_{i\text{-}} = (\Delta H^*/k_bT) - q(\Delta S^\circ/k_b + \ln\Phi + \ln E) \tag{21}$$

from which

$$\mathrm{d}\ \ln t_i/\mathrm{d}\ \ln E = -q. \tag{22}$$

In addition this treatment suggests that ΔH^* for the induction period should be independent of E and that q should be temperature invariant.

Induction periods were measured[34] as a function of relative exposure level, E_{rel}, and temperature for the same solvent-based, pre-formed constructions for which the data of Tables I and II were obtained. The induction period data from Ref. 34 with ΔH^* calculated according to Eq. (20) and with q calculated according to Eq. (22) are reported in Table III. These results show:

(a) Eq. (22) is valid, i.e., the ln–ln relationship is indeed linear;

(b) the transmission coefficient is, within experimental error, temperature independent; and

(c) within experimental error, ΔH^* for the induction period is exposure independent,

all as expected from the theoretical treatment outlined above. It follows from the treatment that selectivity in development, i.e., the ability to discriminate image and fog, is of entropic origin in this type of photothermographic material.

Figure 2 shows in schematic fashion how the characteristics described above function to define the exposure-dependent response of the photothermographic medium. Accordingly the left panel shows a series of optical density versus development time, t, traces corresponding to a series of exposures. For a given development time, t_{dev}, the obtained density values can be projected onto the D–log$E$ plot, shown as the right panel of the Fig. 2. For the geometry illustrated and Eq. (22), it can be shown that the slope, γ, of the linear portion of the characteristic curve resulting under typical development conditions where $t_{dev} > t_i$ and $q < 1$, is given by

$$\gamma = -2.303(D_{max} - D_{min})kqt_o \tag{23}$$

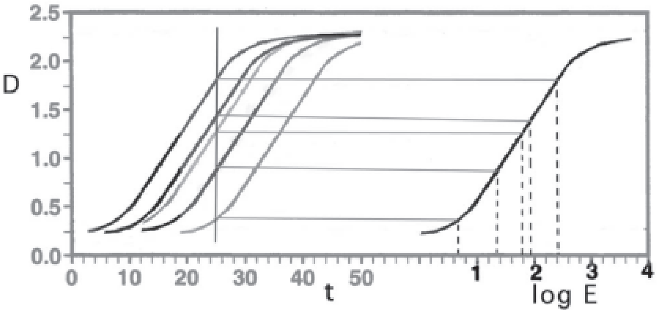


Figure 2. Schematic for evolution of the characteristic curve in a solvent-based photothermographic film. On the left are shown representative kinetic traces for development (D vs. t) of a series of photothermographic samples corresponding to various exposure levels, E; exposure increases from right to left. At a given development time, 25 sec in this case, indicated by the vertical line, a unique $D(E)$ is obtained; these values can be projected, as indicated by the horizontal lines, onto the D–log$E$ plane, shown in the right half of the figure, to generate the photothermographic characteristic curve.

where k is the pseudo-first order rate constant for development continuation (related to the autocatalytic rate constant by Eq. (2)). Also t_o represents a hypothetical induction period corresponding to the condition where only one latent image center is formed per sphere of development, and which appears in the derivation of Eq. (23) as a constant of integration. Note that Eq. (23) predicts that γ is independent of t_{dev} but temperature dependent, insofar as k describes an activated process, under these conditions.

Water-Based Photothermographic Media

Much less is known about the mechanism of development in water-based photothermographic materials. It has been observed that number density of developing centers increases with exposure,[36] as in the solvent-based case, even though secondary nucleation apparently does not occur during the course of development with these materials. This result suggests that in water-based media, as in their solvent-based counterparts, development selectivity has an entropic origin. It is also known that in these materials size of individual silver deposits, rather than number density, increases with development time,[4,36] and that the rate of silver development is reaction limited. This latter insight has enabled useful application of development accelerator technology in this case.[4]

By analogy to conventional silver halide materials where these conditions obtain,[47] application of autocatalytic kinetics to thermal development in water-based systems should be appropriate. Thus

$$(1/a_o)\ln(x/x_o) = k_{auto}t \tag{24}$$

where a_o is the concentration of the excess reagent, developing agent in this case, x is the activity of the autocatalytic product, silver in the present case, at time t, and x_o is the initial activity. The meaning of x_o requires some elaboration. Classical phase formation theory[51,80] defines "germ nuclei" as potential nucleation sites which can be converted to "growth nuclei", i.e., catalytically active sites, by some initiating step, e.g., light exposure, in which case the "growth nuclei" correspond to latent image centers.. Let the number density of such germ nuclei be N_o, then

$$x_o = 2[N(E)/N_o]/\{1 + [N(E)/N_o]\} \tag{25}$$

(which has the same functional form as the Langmuir adsorption isotherm) and, for $N(E) < N_o$, approximately

$$x_o = 2[N(E)/N_o] \tag{25a}$$

where $N(E)$ is defined by Eq. (17). Combining Eqs. (17), (24) and (25) yields

$$\ln(xN_o/2\Phi E) = a_o k_{auto} t, \tag{26}$$

from which we infer that development rate should exhibit exposure dependence. This phenomenon is well known for conventional silver halide materials with typical hydroquinone developers.[53] A corollary to this inference is that in these materials image contrast increases with development time, unlike the case of the solvent-based photothermographic materials, but typical of conventional silver halide development with, e.g., hydroquinone,[53] Metol-hydroquinone or Phenidone™ hydroquinone[54] developers.

Sufficient experimental data on the kinetics of development of water-based photothermographic materials are not available in the literature at the present time to evaluate these predictions rigorously. Qualitatively similar predictions have been made, however, using the semiempirical model of Ito et al.[37]

Conclusions

We have reviewed and analyzed recent research on the chemistry of development of grayscale, silver carboxylate-based photothermographic imaging media. It is now generally accepted that all image silver comes from the silver carboxylate phase. The overall reaction scheme encompasses the steps of dissolution of silver carboxylate by action of silver complexing agents. The resulting soluble complexes, particularly silver(I) phthalazine complexes, then diffuse to a reaction center, initially provided by latent image, in a medium comprising molten carboxylic acid (byproduct of the complexation reaction) or binder, highly plasticized by the carboxylic acid. The diffusion range creates a "sphere of influence", which can be observed by TEM, surrounding the development center in solvent-based materials. A corresponding sphere of influence is not necessarily observable in water-based materials, however.

Morphological studies of developed silver suggest: (a) two stages of development giving rise to filamentary and dendritic silver deposits, respectively, and (b) in solvent-based (but not water-based) media a considerable degree of secondary nucleation, occurring over the course of the reaction. Thermal development follows autocatalytic kinetics, and exhibits a large activation enthalpy, along with a positive entropy of activation; both parameters are inconsistent with a diffusion limited rate of development. In the solvent-based systems studied, secondary nucleation has been proposed to provide positive feedback and be rate-determining, consistent with modern theories of phase formation and crystallization. Both solvent-based and water-based systems exhibit exposure dependent induction periods, which suggest an entropic basis for photocatalysis of image development.

The electrochemistry of hindered phenolic developing agents has been studied. Two-electron oxidation is characteristic of these compounds, with a deprotonation step, which is rate determining, occurring between the two single electron transfers. Thus silver ions may be reduced in pairs, which would facilitate the secondary nucleation process.

With knowledge of development kinetics it is possible to construct phenomenological models for the characteristic curves of photothermographic media. In solvent-based materials operation of secondary nucleation results in a development rate, subsequent to the induction period, that is exposure independent, and contrast is independent of development time. On the other hand the models predict that development rate is exposure dependent for water-based materials, and that contrast increases with development time.

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